WORLD BIOENERGY 2008

Conference & Exhibition on Biomass for Energy

27 - 29 MAY 2008, JÖNKÖPING - SWEDEN

www.worldbioenergy.se

PROCEEDINGS POSTER SESSION

THE ROLE OF LIMESTONE IN PREVENTING AGGLOMERATION AND SLAGGING DURING CFB COMBUSTION OF HIGH-PHOSPHOROUS FUELS

Barišić V.[1], Åmand L.-E.[2], Coda Zabetta E.[3]
[1]Foster Wheeler Energia Oy, Relanderinkatu 2, FI-78201 Varkaus, Finland,
Phone: +358 (0)10 393 7514; Fax: +358 (0)10 393 7689; e-mail: vesna.barisic@fwfin.fwc.com
[2]Chalmers University of Technology, Energiteknik 4, SE-412 96 Göteborg, Sweden
Phone: +46317721439; Fax: +46 31 772 35 92; e-mail: lars-erik.amand@chalmers.se
[3]Foster Wheeler Energia Oy, Relanderinkatu 2, FI-78201 Varkaus, Finland,
Phone: +358 (0)10 393 7845; Fax: +358 (0)10 393 7689; e-mail: edgardo.coda@fwfin.fwc.com

ABSTRACT: This paper presents key observations on the role of limestone in preventing bed agglomeration during combustion of a high-phosphorous fuel in CFB boilers. Composition of the bed material samples were analyzed using X-ray fluorescence, and scanning electron microscope combined with an energy dispersive X-ray analyzer (SEM/EDXA). It has been demonstrated that during combustion of the high-phosphorous fuel under CFB conditions, addition of limestone reduces or prevents bed agglomeration and formation of slag by interfering with the ash chemistry, and not by simple dilution of the reacting system. The role of limestone can be summarized as: 1) to provide calcium for the reaction with phosphorous forming high-temperature-melting calcium phosphates instead of low-temperature-melting potassium phosphates, and 2) to coat silica particles preventing the reaction of potassium (calcium) phosphates and silica originating from the fluidizing sand, which can form low-temperature-melting potassium (calcium) silicates, especially relevant for fluidized bed combustion conditions.
Keywords: agricultural residues, phosphorous, circulating fluidized bed (CFB), agglomeration, limestone

1 INTRODUCTION

Utilization of biomass fuels in energy production continues to grow worldwide as a response to climate change concerns induced by anthropogenic emissions of CO_2. In addition to wood derived fuels and herbaceous biomasses, an increased interest can be observed towards the utilization of residues from food industry and the residues from production of bio-derived fuels for the transport sector (i.e. biodiesel). Seeds (rapeseed, sunflower, etc.) and cereal grains (barley, rye, wheat) are all among "opportunity" fuels that have been considered as an addition to, or partial replacement of fossil fuels for power generation. Common characteristics for these types of biomass fuels are:

- Nitrogen content is very high,
- Sulfur content is higher than for wood derived biomass, but lower than for bituminous coals,
- Chlorine content varies from very low to very high,
- Ash content is higher than for wood derived fuels, but lower than for bituminous coal, and
- Ash is composed predominantly of alkali and earth-alkali elements, and phosphorous.

A fuel with such composition is expected to induce ash-related problems during combustion, and possibly high nitrogen oxide and hydrogen chloride emissions. Focusing here only on ash-related problems, very high phosphorous content (0.74–0.83 $wt\%_{d.s.}$) together with high potassium content (0.57–0.71 $wt\%_{d.s.}$) was found to be a critical quality responsible for slag formation during the combustion of cereal grains in fixed-bed cereal burner [1]. The slag was attributed to the formation of low-temperature-melting potassium phosphates. Projected on fluidized bed combustion technology, high-phosphorous fuels are therefore expected to induce bed agglomeration. Lindström at al. [1] demonstrated that addition of lime can reduce the formation of slag due to formation of high-temperature-melting calcium potassium phosphates.

Foster Wheeler together with Chalmers University of Technology has tested the combustion properties of another high-phosphorous fuel, rapeseed residue, in a 12 MW_{th} CFB boiler. The high-phosphorous residue originated from biodiesel production from rapeseed, and it was co-fired with wood (12%, 21%, and 45% on energy basis). Even though, as compared to cereal grains, rapeseed residues have higher content of calcium in the fuel, which is expected to help against formation of slag and bed agglomeration, a boiler shut down occurred after 12 hours of operation due to an intense agglomeration leading to defluidization. With the intention to minimize agglomeration by capturing phosphorous, limestone was added. As projected, with limestone present the boiler operation was successful for 12 hours, and agglomeration was no longer detected. The role of limestone in preventing bed agglomeration during combustion of high-phosphorous fuel in CFB combustion conditions has been studied, and the details are reported in this paper.

2 EXPERIMENTAL

Co-combustion tests of rapeseed residue with wood have been performed at a 12 MW_{th} CFB boiler at Chalmers University of Technology, Göteborg, Sweden. The boiler is build for research purposes, but it has all the features of a small-scale commercial boiler for heat production. Details of the boiler are given elsewhere [2].

Fuels used in the co-combustion tests were: rapeseed cake pellets, residue from biodiesel production located in Denmark; wood pellets, produced from pre-dried saw dust of pine and spruce; and wood chips, stem wood produced from spruce. The fuel properties are summarized in Table I.

Rapeseed cake pellets (RCP) were co-fired with wood pellets (WOP) and wood chips (WOC) in proportions as indicated in Table II, without and with addition of limestone. These tests were performed in connection to the tests described in [3]. At the end of each test the following samples were collects: bottom ash (BA), circulating material (CM), fly ash from secondary cyclone (FASC), and fly ash from baghouse filter (FABF). The composition of samples was analyzed using X-ray fluorescence, and scanning electron microscope combined with an energy dispersive X-ray analyzer (SEM/EDXA). Crystallography of the bed material samples was analyzed by X-ray diffractometry; however, the results were deemed not reliable, and will not be included here.

Table I: Fuel Properties

Analysis	Rapeseed Cake Pellets*	Wood Pellets	Wood Chips
Ash at 550°C [wt%$_{d.s.}$]	7.5	0.6	0.7
Ultimate analysis [wt%$_{d.s.}$]			
Carbon	49.9	50.2	49.5
Hydrogen	6.9	6.0	6.2
Nitrogen	5.10	0.06	0.15
Sulfur	0.72	0.01	0.02
Chlorine	0.26	0.02	0.01
Oxygen, calculated	29.6	43.4	43.8
LHV, as received [MJ/kg]	18.88	17.21	8.76
Ash forming elements [mg/kg$_{d.s.}$]			
Sodium	4660	45	32
Potassium	12300	828	757
Calcium	7040	912	1521
Magnesium	4500	178.8	233
Silicon	43.4	40.2	24
Aluminum	152	52.8	13
Iron	261	696	120
Titanium	3.6	2.4	1
Phosphorus	11500	78	113

*as reported in [3]

Table II: Test parameters

Test	Fuel[1]	Fuel ratio, % on energy basis	Test duration [hour]
		12 + 24 + 64	4
1	RCP + WOP + WOC	21 + 22 + 57	4
		45 + 16 + 39	4
2	RCP + WOP + WOC + limestone	12 + 38 + 50	12

[1]RCP – rapeseed cake pellets, WOP – wood pellets, WOC – wood chips

3 RESULTS AND DISCUSSION

The elemental composition of ash samples taken at the end of Test 1 (without limestone), and Test 2 (with limestone addition) is shown in Figure 1. The elemental composition is expressed as oxides of silicon, sodium, potassium, calcium, magnesium, phosphorous, and sulfur, plus chlorine. The unseen balance to 100 wt% includes oxides of aluminum, iron and titanium, plus carbon.

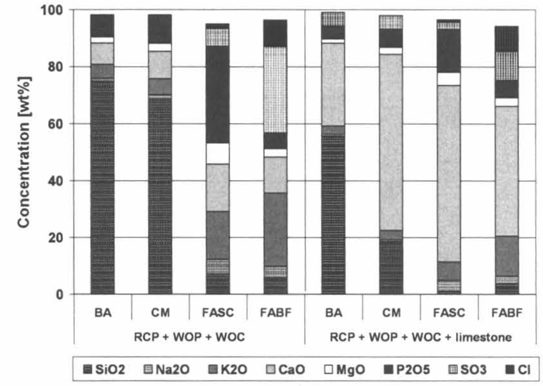


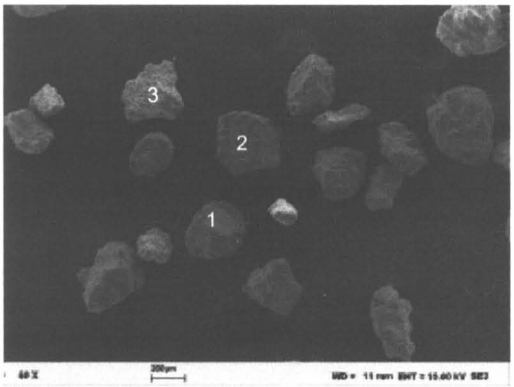
Figure 1: Composition of bottom ash (BA), circulating material (CM), fly ash from secondary cyclone (FASC) and fly ash from baghouse filter (FABF) collected at the end of co-combustion tests of rapeseed cake pellets (RCP) with wood pellets (WOP) and wood chips (WOC), without and with limestone addition.

As can be seen from Figure 1, when limestone was not added (Test 1, samples RCP + WOP + WOC), bottom ash as well as circulating material accumulated ash-forming elements from rapeseed cake pellets, i.e. Na, K, Ca, Mg and P. Sulfur was not captured in the bed, and sulfates were found only in fly ash samples. Also chlorine, as usual, was found only in the fly ash samples.

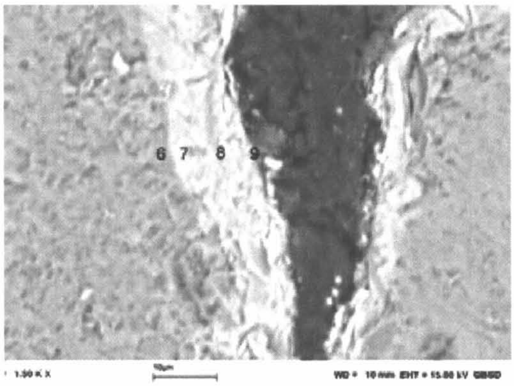
As expected, addition of limestone (Test 2, samples RCP + WOP + WOC + limestone) caused an increase in calcium and a corresponding decrease in silicon in all samples. Additional calcium from limestone promoted sulfur capture in the bed.

Besides the common effects described above, the addition of limestone had other useful consequences, which were investigated in detail by SEM/EDXA. Figures 2–5 illustrate the key observation of such investigation. Figure 2 shows typical micrographs of samples collected after the test without limestone addition. On these micrographs are numbered selected spots onto (a) surface and (b) cross-section of the depicted particles. Corresponding EDX analyses of the numbered spots are shown in Figure 3. Similarly, Figures 4 and 5 show SEM micrographs and EDX analyses of samples collected after the test with limestone addition.

When limestone is not added (Figures 2 and 3) the bed material is made of mostly sand particles (principally SiO_2), which are coated with K, Ca, P, Na, and Mg (ash-forming elements from rapeseed cake). Silicon (Si) is a major part of the coating layer. There is a small amount of sulfur in the coating, which is revealed only by SEM/EDX surface analysis. Bed material with such coating was found to be sticky and to form agglomerates.

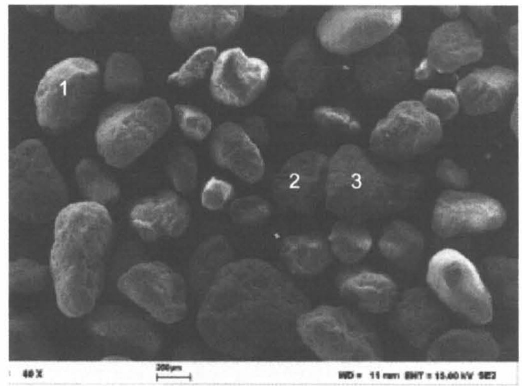


(a) CM_RCP + WOP + WOC (surface)

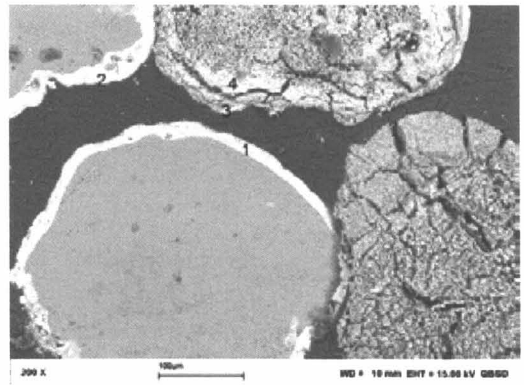


(b) CM_RCP + WOP + WOC (cross-section)

Figure 2: SEM micrographs of circulating material (CM) samples from co-combustion of rapeseed cake pellets (RCP) with wood pellets (WOP) and wood chips (WOC): (a) surface and (b) cross-section.



(a) CM_RCP + WOP + WOC + limestone (surface)



(b) BA_RCP + WOP + WOC + limestone (cross-section)

Figure 4: SEM micrographs of circulating material (CM) and bottom ash (BA) samples from co-combustion of rapeseed cake pellets (RCP) with wood pellets (WOP) and wood chips (WOC) with limestone addition: (a) surface and (b) cross-section.

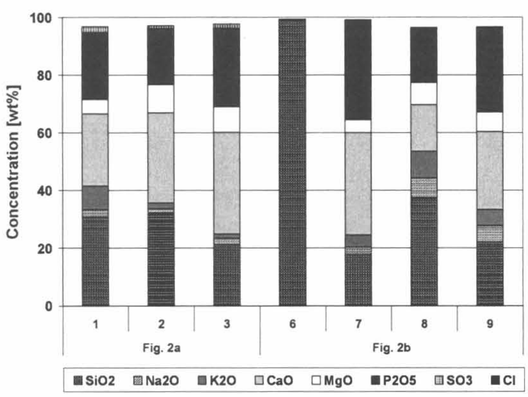


Figure 3: EDX spot analysis of particles shown in Figure 2.

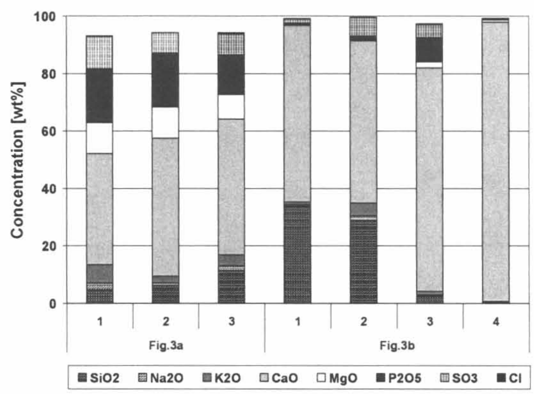


Figure 5: EDX spot analysis of particles shown in Figure 4.

When limestone is added (Figures 4 and 5) the bed material is made of (i) lime particles that have captured phosphorus together with capturing sulfur, and (ii) sand particles with a coating layer richer in Ca and S compared to the coating of samples when limestone is not added. Bed material with such composition did not form agglomerates.

Additional SEM/EDX analysis was also performed on the surface of agglomerates sampled during the boiler inspection after the shutdown, which occurred when firing mixture of rapeseed cake pellets and wood without limestone. The results are shown in Figures 6 and 7. Similarly to samples of bottom ash and circulating material, the surface of agglomerates is composed of ash elements from rapeseed cake pellets (Na, K, Ca, Mg, P) and silica. However, higher amount of alkali and silica were measured on the surface of agglomerate compared to the surface of bottom ash and circulating materials from co-combustion of rapeseed pellets and wood.

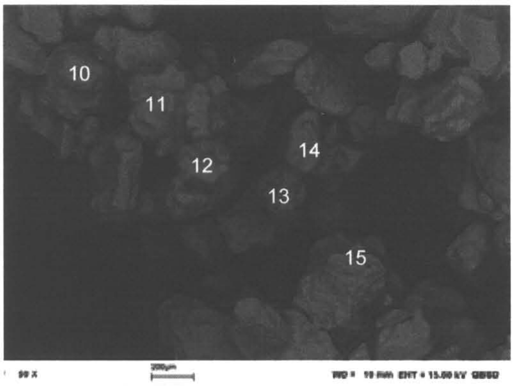


Figure 6: SEM micrographs of an agglomerate formed during the co-combustion of rapeseed cake pellets with wood, pellets and chips, without limestone addition.

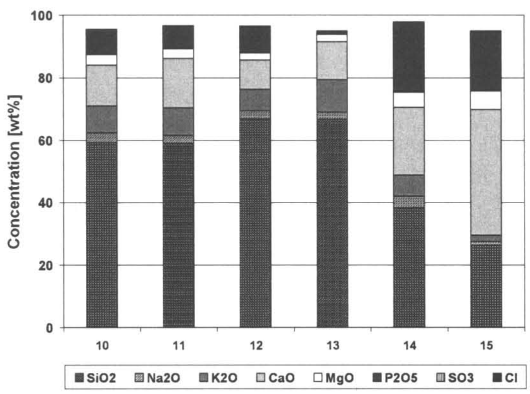


Figure 7: EDX spot analysis of particles shown in Figure 7.

The findings summarized above indicate that agglomeration and slagging during combustion of high-phosphorous plus high-alkali fuels can occur as a results of two phenomena: (i) accumulation of low-temperature-melting salts of potassium and phosphorous, and (ii) in the presence of silica from sand and calcium from fuel, potassium phosphate can react with silica forming low-temperature-melting silicates of potassium and calcium while phosphorous bounds with calcium.

While the first phenomenon is known from recent literature [1], the second phenomenon is not acknowledged and therefore it was further verified in laboratory conditions. A sintering test was conducted according to Foster Wheeler's method on several mixtures of following chemicals: K_3PO_4, $Ca_3(PO_4)_2$, KCl, and SiO_2. Sintering occurred in all systems containing K_3PO_4, and the presence of SiO_2 made the sinters harder compared to cases when silica was not present.

The sintering test results corroborate the existence of the second phenomenon especially in fluidized bed conditions, and reinforce the theory that limestone addition can reduce agglomeration and slagging by providing lime, which coats sand particles, thus preventing reactions between silica and potassium phosphate. Therefore, in combustion of fuels with elevated content of alkali and phosphorous, the limestone would not simply dilute the concentration of problematic species, but would actively interfere with their chemistry. Such effect could allow mitigating agglomeration and slagging with relatively small amounts of limestone when firing fuels with elevated contents of phosphorous.

4 CONCLUSION

During combustion of fuels that contain high potassium and high phosphorous level, such as rapeseed residues, the following mechanisms may occur:

1) Formation of low-temperature-melting potassium phosphates, which may cause agglomeration, sintering, and slagging regardless the combustion technology, and
2) Formation of low-temperature-melting potassium silicates in the presence of SiO_2 and Ca, especially under fluidized bed conditions. Potassium silicates cause rapid formation of hard agglomerates, harder than the agglomerates formed by mechanism 1. In the reaction of SiO_2 from fluidizing sand and potassium phosphate, potassium silicate is formed while phosphorous bounds to calcium forming stable high-temperature-melting calcium phosphates. This reaction is enhanced if alkali chlorides are present, and in that case HCl is released.

Foster Wheeler together with Chalmers University of Technology has tested a method to minimize/eliminate agglomeration, sintering, and slagging during combustion of high-phosphorous fuels in fluidized bed conditions, and that is to add limestone.

The role of limestone can be summarized as:
a) Addition of lime causes increase in calcium concentration in the system, which leads to the formation of high-temperature-melting calcium-potassium-phosphate and sulfate phases.
b) Addition of lime prevents reactions of potassium phosphate and silica by coating the silica particles, and as a result taking out silica from the reacting system.

Mechanism 1 and role of limestone (a) are described by Lindström et al, 2007 [1]. Signs for occurrence of mechanism 2 and role of limestone (b) can be speculated from literature [4-6], however, the mechanism and the role of limestone are not explicitly described.

At the present time, thermodynamic data that should be used to simulate the system $CaO\text{-}K_2O\text{-}P_2O_5\text{-}SiO_2$ are not accurate or not even available.

To conclude, it has been demonstrated that agglomeration of the bed material that occurs during co-combustion of high-phosphorous high-alkali fuels with wood in fluidized bed boilers can be avoided or minimized by adding limestone. Limestone provides calcium for the reaction with phosphorous forming high-temperature-melting calcium phosphates instead of low-temperature-melting potassium phosphates, and coats silica particles preventing the reaction that would form low-temperature-melting potassium (calcium) silicates.

6 REFERENCES

[1] Lindström, E.; Sandström, M.; Boström, D.; Öhman, M. Slagging Characteristics during Combustion of Cereal Grains Rich in Phosphorus. Energy Fuels 2007, 21, 710-717.

[2] Åmand, L-E. Leckner, B. Metal Emissions from Co-Combustion of Sewage Sludge and Coal/Wood in Fluidized Bed, Fuel 2004, 83, 1803-1821.

[3] Piotrowska, P., Zevenhoven, M., Hupa, M., Davidsson, K., Åmand, L.-E., Kassman, H., Coda-Zabretta, E. Fate of Alkali metals During Co-Combustion of BioDiesel Residues with Coal in a Semi-Industrial CFB Boiler. 9th International Fluidized Bed Conference, Hamburg, Germany May 2008.

[4] Bishop S. Earl. Treatment of Phosphate Rock. UNITED STATES PATENT AND TRADEMARK OFFICE GRANTED PATENT, Nov 1916, Patent No. US1204238.

[5] Sørensen et al. A Method for Reducing Agglomeration, Sintering and Deposit Formation in Gasification and Combustion of Biomass. PATENT COOPERATION TREATY APPLICATION, Jan 2001, Patent No. WO0105911.

[6] Llorente et al. Ash behavior of lignocellulosic biomass in bubbling fluidized bed combustion. Fuel 2006, 85, 1157-1165.

7 ACKNOLEDGEMENTS

This work has been carried out as a part of the SAFEC project, and the financial support of TEKES is acknowledged. Tor Laurén is kindly acknowledged for his help with the SEM/EDX analysis. The authors would like to express special gratitude to Prof. Rainer Backman for fruitful discussions. The tests at the research boiler were performed by additional support by the Swedish Energy Administration that is gratefully acknowledged. The practically performance of the tests were carried out by the operational staff employed by Akademiska Hus and by research engineers from Chalmers University of Technology.